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The
Reaction between Manganese Dioxide
and
Potassium Permanganate.

Dissertation
presented for the degree of Doctor of Philosophy to the Board of University Studies of the Johns Hopkins University
by
Arthur John Hopkins.

1893.

Acknowledgment

The work recorded in this paper is the result of a suggestion given by Professor H. N. Morse. It has received his careful attention throughout its course. For his instruction and exact criticism, I wish to offer my acknowledgment and thanks. I wish also to express to Professor Ira Remsen my appreciation of his interest and instruction and to offer to Dr. J. S. Ames my thanks for his instruction in Physics —

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Introduction.

The usual laboratory solution of potassium permanganate must be frequently restandardized. A slight loss in strength may be detected after standing over a few days and this change becomes more rapid as the decomposition proceeds. When one looks for the cause of this increase in the rate of the decomposition of K. permanganate the attention is naturally directed to the brown manganese oxide

which separates from the solution. A desire to ascertain whether the presence of this oxide influences the rate of the decomposition suggested the experiments here described.

The fact that potassium permanganate may react with certain so-called peroxides with evolution of oxygen has long been known and it appeared possible that a similar reaction may take place between manganese dioxide and potassium permanganate.

Morse and Allen investigated the reaction between lead dioxide and potassium permanganate and there is embodied in Allen's dissertation(1) a statement of the earlier work in this line with references to the literature on the subject.

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(1) Johns Hopkins University [illegible].

They have shown that in the presence of a quantity of dilute nitric acid which is equivalent to the potassium in the potassium permanganate used, lead dioxide reduces the permanganate to manganese dioxide without itself suffering reduction, while in the presence of an excess of stronger nitric acid, e.g. normal to eight normal, the lead dioxide is also reduced.

The following equations represent the reactions referred to:

I, when the nitric acid is equivalent to the potassium in the potassium permanganate,

$$2\,KMnO_4 + 3\,PbO_2 = K_2O + 3\,PbO_2 + 2\,MnO_2 + 1\tfrac{1}{2}\,O_2.$$

II, when the nitric acid is in excess,

$$2\,KMnO_4 + 3\,PbO_2 = K_2O + 3\,PbO + 2\,MnO_2 + 3\,O_2.$$

The reducing action of manganese dioxide upon potassium permanganate was suspected from the observed increase in the rapidity of the decomposition of potassium permanganate solutions. But only a suggestion of such a reaction could be found in the literature. Thénard,(1) in 1856 states that manganese dioxide may act upon potassium permanganate either as a reducing agent, in which act the manganese dioxide is changed to a manganate, or its influence may be catalytic, causing the evolution of oxygen. Again Mulder(2) in 1858, ascribed the decomposition of potassium permanganate solutions to the presence of some potassium manganate.

It could not be ascertained that any investigation of this matter had ever been

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(1) Comptes Rendues 42, 382

(2). Jahresbericht 1858 p.58

undertaken. It was therefore decided to study the question and it appeared that the most satisfactory evidence could be obtained by measuring the quantity of oxygen which is evolved when potassium permanganate and manganese dioxide are brought together.

Description of Apparatus.

The apparatus(1) employed in this work consists of four parts:

" I) a flask, A, in which the reactions were conducted. A melting point bulb of about 40 cc. capacity, the diameter of its neck being 20 mm., was used for this purpose.
This was closed with a two-hole rubber stopper, through one hole of which passed

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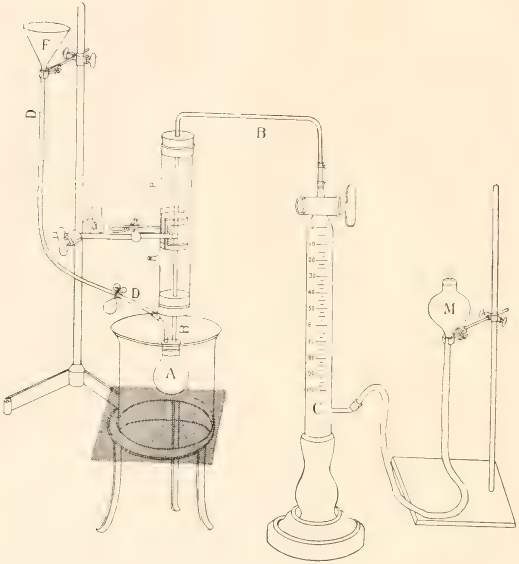
(1) This apparatus was used by Allen and described by him. I wish to acknowledge my indebtedness to him for the illustration and description given here which is taken by permission word for word from his dissertation.


F
D
B
D
B
A
C
M
10
20
30
40
50

2) a small glass tube, BB, running up from the flask about 40 cm., and then bent twice at right angles. The limb of this tube was surrounded by a small Liebig's condenser, while the shorter turned down to meet —

3) a Schiff's azotometer filled with mercury and connected at its top with the tube above mentioned. In practice it was found desirable to have a little water on the top of the mercury column.

4) Through the second hole of the rubber stopper closing the flask was passed a short piece of glass tubing bent obliquely just above the stopper and tightly connected with a rubber tube about 50 cm. long, D.D. This tube was clamped near its lower end with a Mohr's pinch-cock, while the upper was connected with the stem of a small funnel, F.

When an experiment was to be conducted,

the azotometer C, was connected to the tube, B, and tied tightly, a piece of good rubber-tubing being used for the connection. The reservoir of the azotometer, M, was then raised until the mercury had driven out all the air in C, and the stop-cock closed. Next the funnel F was filled with water, the pinch cock closing D opened and the water allowed to flow down and drive out all the air in the tube. The latter was then clamped and thus kept full of water. The apparatus being now ready, the flask A, containing the substances in the desired quantity, was made fast to B and D by means of its stopper. The reservoir M was then lowered and the stop-cock of C opened. The flask A was heated in a water bath for any desired time, the oxygen being collected in C at

fast as ~~fast as~~ it was given off.

At the end of the experiment, all the gases which remained in A and B were driven over into C by lowering the reservoir M and opening the pinch cock at D. When this was accomplished the stop-cock of C was closed and the gases brought under atmospheric pressure by bringing the mercury in C and M to the same level.

It will be seen that in this gas volume was included the air which A and B contained at the beginning of the experiment.

The oxygen evolved from the contents of the flask was determined thus: After reading off the total volume of air and oxygen and reducing to normal conditions, the total volume of oxygen was obtained by absorption with phosphorus or pyrogallol, and from the residual nitrogen could be calculated. The

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volume of air to be deducted from the total volume of gases. The remainder is the volume of oxygen sought."

Action of manganese dioxide on potassium permanganate in acid solution.

Three sets of apparatus like the one described were used.

The flask of apparatus No I contained manganese dioxide and dilute nitric acid,
the flask of apparatus No II contained potassium permanganate and dilute nitric acid.
The flask of apparatus No III contained potassium permanganate and dilute nitric acid and manganese dioxide.

The manganese dioxide used in these experiments was precipitated from a solution of

potassium permanganate by a dilute solution of manganous sulphate in the manner described on page [illegible] and then washed and dried at 100°c.

An illustration of the proportions in which the different substances were brought together in each of the three flasks is to be found in the following statement of the quantities used in the first experiment.

The variations from these proportions occurring in subsequent experiments are noted in the table giving the summary of the results. Usually about 150 m.g. of manganese dioxide were used and the solutions in the three flasks were brought to the same volume by addition of distilled water.

Experiment No I

Flask No I Manganese dioxide 150 m.g.
$\frac{N}{10}$ nitric acid 114.28 c.c. [= Mn

in $KMnO_4$ in No II or No. III]

Water, 27.12 c.c. [Total solution =
41.40 c.c.]

Flask No. II

Potassium permanganate, 20 c.c. =
112.48 m.g. $KMnO_4$.

$\frac{N}{10}$ nitric acid 7.14 c.c. [≡ K in $KMnO_4$]

Water, 14.26 c.c. [Total solution =
41.40 c.c.]

Flask No III

Potassium permanganate, 20 c.c. = 112.48 m.g.
$KMnO_4$

$\frac{N}{10}$ nitric acid 21.40 c.c. [≡ K+Mn in
$KMnO_4$]

Manganese dioxide 150 m.g.

The nitric acid in No I is calculated to be the same as that remaining free after the potassium of the permanganate in No. III has been neutralized. It will be seen

that the quantities of free nitric acid are the same in flask No I and in flask No III provided the potassium of the permanganate is appropriated by the nitric acid. Moreover each flask contains the same quantity of manganese dioxide and the volume of the liquid is the same in both.

On the other hand flask No. III contains permanganic acid. This arrangement was selected in order to determine how far the evolution of oxygen was influenced by the action of nitric acid on the manganese dioxide or by the spontaneous decomposition of permanganic acid. It was thought that if more oxygen should be obtained from flask No. III containing a mixture of permanganate, manganese dioxide and nitric acid, than from mixtures No I and No II, the larger volume

must be due to the reduction of the permanganate by the manganese oxide.

The three flasks after having been filled as described were attached to the apparatus and then all submerged to the same depth in the boiling water of a single glass water bath. The stop cocks of the azotometers were then opened and the mercury allowed to fall to within about fifty millimetres of its level in the reservoirs. This difference in level was maintained as nearly as practicable by lowering the reservoirs commensurately with the increase in gas volume. No action could be observed in flasks No I and No II during the whole course of the experiment. The contents of flask No III however gave off bubbles of oxygen immediately, the mercury fell in the azotometer and the dark purple of the permanganate solution in flask No. III

became rapidly lighter. Within about five minutes it was reduced to a delicate pink but this tint persisted for about ten minutes when it also disappeared. Immediately after the disappearance of the permanganate color the solution was filled with a brown oxide which remained for about thirty five minutes when it subsided leaving the supernatant liquid clear. Notwithstanding the fact that the color of the permanganate had entirely disappeared and the suspended oxides had subsided within an hour after beginning the experiment, the flasks in the earlier experiments were allowed to remain for two hours longer. By admitting distilled water through the tube D [see figure] the gas was then forced over into the azotometer. Finally the oxygen was determined in the manner previously

described

The following illustration from the first experiment may serve to show the method of calculating the results.

	I	II	III
Total air and oxygen	= 42.60 c.c.	52.40 c.c.	60.60 c.c.
Nitrogen after absorbtion of oxygen	= 34.00 c.c.	40.90 c.c.	37.80 c.c.
Oxygen	= 8.60 c.c.	11.50 c.c.	22.80 c.c.

Air = 79.8% nitrogen
20.2% oxygen

Oxygen of air = Nitrogen found $\times\frac{20.2}{79.8}$	= 8.60 c.c.	10.353 c.c.	9.57 c.c.
Oxygen obtained	= 0.0	1.147 c.c.	13.23 c.c.

Temperature = 21°C.

Barometer = 737 m.m.

Oxygen obtained at normal	= 0	1.033 c.c.	11.913 c.c.

The 20 c.c. $KMnO_4$ = 112.48 m.g.

1 atom of oxygen = 7.967 c.c.

Atoms oxygen found
from one molecule $KMnO_4$ = 0   0.129   1.496

As at the end of the preceding calculation the results are expressed in the table following in terms of oxygen atoms obtained from each molecule of potassium permanganate ($KMnO_4$) reduced. Thus an equivalent of one atom of oxygen from one molecule of potassium permanganate would equal $\frac{15.96}{157.67}$ of the weight of potassium permanganate used in the experiment. This weight divided by the weight of one cubic centimetre of oxygen gives the number of cubic centimetres of oxygen at normal equivalent to one atom of oxygen from one molecule of potassium permanganate. The results obtained are tabulated as follows:

Three-hour determinations.

	Flask I		Flask II		Flask III	
	MnO_2 [150 m.g.]	$\frac{N}{10} HNO_3$ No. of molecules	$KMnO_4$ 20c.c. = 112.48 m.g.	$\frac{N}{10} HNO_3$ No. of molecules	$KMnO_4$ 20c.c. = 112.48 m.g	$\frac{N}{10} HNO_3$ No. of molecules
1	0.00	2	0.13	1	1.495	3
2	0.00	"	?	1	1.493	"
3		"	0.13	3	1.532*	"
4	0.00	"	0.21	"	1.466	"
5	0.03	"	0.10	"	1.467	"
6	0.02	"	0.25	"		"
7	0.06	"	0.08	"	1.520*	"
8	0.04	"	0.15	"	1.527	"
9	0.04	"	0.11	"	1.504	"
10		"	0.20	"	1.504	"
11	0.03	"	0.14	"	1.516	"
12	0.00	"	0.18	"	1.524	"
13	0.03	"	0.25	"	1.559*	"
14	0.05	"	0.26	"	1.574	

	Flask I		Flask II		Flask III	
15	0.02	1	0.32	2	1.552	2
16	0.03	"	0.31	"	1.583(?)	"
17	0.04	"	0.31	"	1.572	"
18	0.01	"	0.32	"	1.466	"
19	0.00	"	0.18	"	1.412	"
20	0.01	"	0.36	"	1.411	"
21	0.06	"	0.22	"	1.402	"
22	0.00	"	0.30	"	1.495*	"
23		2	0.08	3	1.469	3

(1) Fifty minute determinations

24	0.04	1	0.06	2	1.564	2
25	0.04	"	0.11	"	1.491	"
26	0.05	"	?	"	1.572	"
27	0.03	"	0.05	"	1.532	"

(2) Fifteen minute determinations

28	0.05	1	0.08	2	1.340	"
29	0.04	"	0.05	"	1.325	"
30	0.06	"	0.05	"	1.335	"
31	0.00	"	0.00	"	1.347	"

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(1) This marked the time when the oxides first settled, leaving a clear colorless supernatant liquid. (2) This marked the time

	Flask I		Flask II		Flask III	
32	0.03	1	0.03	2	1.412	2
33	0.02	2	0.02	3	1.363	3
34	0.02	"	0.06	"	1.377	"
35	0.00	"	0.02	"	1.363	"

Inspection of the table will show that whether the oxygen were determined immediately after the subsidence of the oxides (i.e. after fifty minutes) or after three hours the results obtained are practically the same. The tendency of the potassium permanganate to lose strength made the frequent preparation of new samples advisable. Wherever a new sample has been used in the course of the experiments, the fact has been noted in the table by an asterisk. It will be noticed that where a new solution is used the figures for flask no. III are immediately larger and nearer to one and one half atoms of oxygen when the solution was first decolorized.

from each molecule of potassium permanganate.

A phosphorus gas-pipette was used for the absorption of the oxygen in all the experiments the results of which are embodied in the foregoing table. In subsequent experiments an alkaline solution of pyrogallol was employed. It is now known that the variation in the composition of the manganese oxide in use had some influence upon the results.

It has also been found that manganese dioxide prepared by the reduction of permanganate by manganese sulphate is much less stable than was supposed at the time this work was begun. The dioxide prepared in this way begins immediately to lose oxygen spontaneously but recovers the same in the presence of an excess of potassium permanganate. In the light of these facts it is easy to understand why lower results were obtained when the oxygen was

determined immediately after the disappearance of the color of the permanganate and before the suspended oxide had subsided. It appears that the manganese oxide employed in these experiments was not, as was supposed at the time, the dioxide but one containing a smaller proportion of oxygen. If such is the case the first action of the permanganate upon it would be to replace the oxygen which had been lost. The reduction of the remaining permanganate would then probably be in accordance with the equation,

$$2KMnO_4 + 3MnO_2 = 2K_2O + 5MnO_2 + 1\tfrac{1}{2}O_2.$$

At the time when the permanganate color disappears, all of the manganese is in the dioxide condition and the further evolution of oxygen, which is shown by the preceding experiments to take place during the subsidence of the suspended oxides, is due to a partial reduction

of this manganate. Therefore the relation of the reduction of the manganese oxide below the unco-conditions before the treatment with permanganate to the reduction which follows the disappearance of the permanganate color will determine whether the oxygen evolved shall be more or less than one and one half atoms to each molecule of permanganate.

Neither variations in the quantities of nitric acid used (from two to three molecules in No III.) nor the very slight variations in the amount of manganese dioxide used, seem to affect appreciably the amount of oxygen obtained.

It appears that the action of manganese dioxide on potassium permanganate is the same as that of lead superoxide (1) in the presence of very dilute nitric acid. Both reduce it to manganese dioxide with the evolution of oxy-

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(1) Allen's thesis.

and one half atoms of oxygen to each molecule of the permanganate.

The evolution of oxygen from flask no. 1 containing manganese dioxide and nitric acid is very slight. From flask no II containing potassium permanganate and one equivalent nitric acid, it is also slight but usually greater than from flask no 1. The differences are much greater in the case of those determinations in which the heating of the flask was continued for three hours and in this fact is to be found further evidence of the reducing action of manganese dioxide on potassium permanganate.

The possibility of a reaction analogous to that between potassium permanganate and manganese dioxide in the presence of strong nitric acid seems to be excluded by the fact that the higher oxides of manganese may be prepared

in the presence of concentrated nitric acid.

Action of a Black Oxide of Manganese on Potassium Permanganate.

As ~~the~~ an analysis of the manganese dioxide showed the probable presence of some manganese in the manganous condition, a sample was treated on the water bath for some days with dilute nitric acid while distilled water was added from time to time to keep the dilution nearly constant. This was done for the purpose of determining whether the manganous manganese might not be extracted in the form of manganese nitrate. The light brown oxide which was used in the previous experiments had been prepared by adding a dilute solution of manganous sulphate

to a hot solution containing potassium permanganate in excess and dilute nitric acid. No analysis of the oxide thus prepared was made at the time of its preparation, but it has been shown by the work of others that the oxide must have had at this time a composition as regards the relation of manganese to oxygen very nearly equivalent to that of MnO_2. During the course of the experiments previously described, a determination of the ratio of the manganese to the available oxygen in the compound was made and found to be as

1.03 : 1.00

The substance gave [illegible] percent manganese and 15.44 percent available oxygen.

A second analysis made some weeks later gave a ratio of manganese to available oxygen of 1.06 : 1.00. —

The substance gave 54.76 percent manganese
15.02 " available oxygen.
The manganese was determined by the method of Gibbs (1) and the available oxygen by oxalic acid and potassium permanganate.
It was this oxide which was treated with nitric acid in the manner described. As the result of this treatment the light brown color changed to black and the oxide became heavier. The dilute nitric acid in which the oxide had been digested was found to contain manganous manganese, but analysis of the black product showed that the oxide had suffered a still further reduction. The ratio of manganese to available oxygen was found to have risen from 1.06:1.00 to 1.157:1.000. The analytical data are given below: —
The substance gave {60.49 percent manganese / 60.46 " "} and

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(1) Silliman's Am. J. Science (2) 44. 216

(15.23 percent oxygen)
(15.19 " ") This oxide would correspond very nearly to a compound having the composition $MnO . 6MnO_2$ but it is by no means certain that the reducing action of nitric acid was finished. The action of this oxide on potassium permanganate was determined under the same conditions as in the case of the brown oxide as described on page [illegible]. The following illustration of the proportions used is taken from the first experiment.

Experiment No. I

Flask No. I Manganese oxide, black, = 150 m.g.
$\frac{N}{10}$ nitric acid = 14.93 c.c. [= Mn in $KMnO_4$ in No. II or No. III]
Water = 27.46 c.c. [Total solution = 42.39 c.c.]

Flask No. II. Potassium permanganate = 20 c.c. = 117.71 m.g.

$\frac{N}{10}$ nitric acid = 22.39 c.c. [= K and Mn in $KMnO_4$] [Total solution = 42.39 c.c.]

Flask No. III. Potassium permanganate = 30 c.c. = 117.71 m.g.

$\frac{N}{10}$ nitric acid = 22.39 c.c. [= K and Mn in $KMnO_4$]

Manganese oxide, black = 150 m.g.

[Total solution = 42.39 c.c.]

The first two results are from experiments in which the action was stopped at the first loss of the color of potassium permanganate. The last two are the results from experiments in which the action was stopped after the oxide had settled leaving a clear colorless supernatant liquid. The amount of oxygen given off in any one case is expressed in the table as the number of atoms of oxygen derived from each molecule of potassium permanganate, as follows:

	Flask I		Flask II		Flask III	
	Black oxide 150 m.g.	$\frac{N}{10}$ nitric acid No. of molecules	Potassium permanganate 20 c.c. = 117.71 m.g.	$\frac{N}{10}$ nitric acid No. of molecules	Potassium permanganate. 20 c.c. = 117.71 m.g.	$\frac{N}{10}$ nitric acid. No. of molecules.
1 2 hours.	0.00	2	0.18	3	1.337	3
2 2¼ hours	0.02	"	0.24	"	1.335	"
3 2½ hours	0.02	"	0.44	"	1.402	"
4 4½ hours	0.00	"	0.55	"	1.362	"

The volume of the oxygen evolved is considerably smaller than that obtained when the brown oxide was used. It is considerably larger than could have been evolved if all of the manganese had been left in the dioxide condition at the close of the experiment. This fact

indicates that there was a slight reduction of the manganese dioxide after the disappearance of the color of the permanganate. That such a reduction of manganese dioxide does take place will be made apparent by a comparison of the results of the first two experiments in which the oxygen was measured soon after the color of permanganate had disappeared, with the results of the last two experiments in which the oxygen was determined after a longer interval. It will be noticed in this as in the series of experiments with the brown oxide that the rate of the evolution of oxygen liberated in flask No. II increases with the time of heating.

The Amount of Nitric Acid neutralized.

A few experiments were made to determine how much nitric acid is neutralized under the conditions which prevailed in the foregoing experiments.

I. The flask contained brown oxide 150 m.g. $\frac{N}{10}$ nitric acid 6.98 c.c. and was heated for three hours in the water bath.

Acid neutralized = 4.51 c.c. = 64.60 percent

II. The flask contained brown oxide 150 m.g. $\frac{N}{10}$ nitric acid 6.98 c.c. and was heated for 50 minutes in the water bath.

Acid neutralized = 3.09 c.c. = 44.20 percent.

III. The flask contained brown oxide 150 m.g. $\frac{N}{10}$ nitric acid 7.46 c.c. and was heated for fifty minutes in the water bath.

Acid neutralized = 3.16 c.c. = 42.30 percent.

IV. The flask contained brown oxide 150 m.g.

$\frac{N}{10}$ nitric acid 7.40 c.c. and was heated for 15 minutes in the water bath.

Acid neutralized 2.70 c.c. = 37.0 percent

V. The flask contained brown oxide 100 m.g.
Potassium permanganate 50 c.c. = 110.48 m.g.
$\frac{N}{10}$ nitric acid 6.98 c.c. (= 2 molecules for 1 molecule $KMnO_4$) and was heated for three hours in the water bath.

Acid neutralized = 0.35 c.c. = 5.0 percent.

VI Repetition of No. V.

Acid neutralized = 0.44 c.c. = 6.3 percent.

VII The flask contained brown oxide 150 m.g.
Potassium permanganate the same as in numbers V and VI and was heated for 15 minutes in the water bath.

Acid neutralized = 5.2 percent.

VIII Repetition of No. VII

Acid neutralized = 4.0 percent

IX The flask contained black oxide 150 m.g.

$\frac{N}{10}$ nitric acid 14.9 c.c and was heated for two and one fourth hours in the water bath.
Acid neutralized 4.87 c.c. = 32.46 percent

X Repetition of No. IX
Acid neutralized = 38.10 percent.

XI The flask contained black oxide 150 m.g. potassium permanganate 20 c.c. = 117.71 m.g., $\frac{N}{10}$ nitric acid 22.39 c.c. (= 2 molecules for each molecule of $KMnO_4$) and was heated four and one half hours in the water bath.
Acid neutralized = 100.00 percent.

No definite conclusions can be drawn from these neutralization experiments since it is well known that manganese oxides prepared as were those used in these experiments always contain some, though probably not a constant quantity of alkali. It is stated by *Bemmelen

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* J. für Prak. Ch. (2) 23, 324 — 379

that manganese dioxide decomposes the salts of the alkalies with liberation of acid.

The Stability of Manganese Dioxide.

Having found in the course of the work already described that manganese dioxide prepared in the wet way is much less stable than was supposed, it was decided to make some experiments upon the spontaneous decomposition which it undergoes. To this end a fresh sample was prepared in the following manner.

10 grams of potassium permanganate were dissolved in 500 c.c. of distilled water and the solution allowed to settle for one day. The liquid was then filtered through glass wool, heated to 60°C. and boiled

with 320 c.c. $\frac{N}{10}$ nitric acid, having also a temperature of 65°C. 20.5 grams of manganous sulphate dissolved in 3.5 litres of water heated to 65°C. were now added, with stirring, to the acidified solution of potassium permanganate. The precipitate was allowed to settle and the supernatant liquid which still retained the permanganate color decanted. The residue was then treated with water, stirred and allowed to settle. The water was decanted and the oxide filtered. The filter used consisted of two platinum cones between which was placed a small paper filter which did not quite reach to the edge of the outer cone. This filter was placed in the bottom of a glass funnel and the oxide poured upon it. The oxide was repeatedly washed with distilled water

and then transferred to a porous plate. It was afterwards heated for several hours to a temperature of 65°C. At this temperature it was found impracticable to bring the oxide to a constant weight, but this fact was no serious obstacle in the way of the subsequent work since it was only desired to ascertain what changes take place in the ratio of the manganese to the available oxygen. The manganese was determined by the method of Gibbs and the available oxygen by oxalic acid and potassium permanganate. An analysis of the oxide made shortly after its preparation in the manner described gave

$$\text{Manganese}\begin{cases}51.98 \text{ percent}\\ 51.74 \quad ''\end{cases} = 51.86 \text{ perct.}$$

$$\text{Oxygen}\begin{cases}14.836 \text{ percent}\\ 14.839 \quad ''\end{cases} = 14.837 \quad ''$$

showing a ratio of manganese to available oxygen of 1.018 : 1.000.

The above analysis was made May 1, 1892. The oxide was then placed in a glass stoppered weighing bottle and allowed to stand until November. An analysis made on the tenth day of the latter month gave a ratio of manganese to available oxygen of

1.198 : 1.000

corresponding very closely to a composition $MnO . 5 MnO_2$. in which the calculated ratio is

1.200 : 1.000

Six months later (April 20. 1893) an analysis of the same material showed a ratio of manganese to available oxygen of

1.300 : 1.000

This result was confirmed by Mr. Walker who made repeated analyses of the substance at the same time.

Another sample of manganese oxide was prepared in the same manner as that used in the previous experiments and placed under water. An analysis made after

Eight days gave a ratio of Mn : available O = 1.01[illegible]:1.000
Twenty " " " " " " " " = 1.037:1.000
Forty three " " " " " " " " = 1.040:1.000

The results here recorded clearly indicate that the brown oxide of manganese which is prepared by the reduction of potassium permanganate by manganese sulphate undergoes a spontaneous decomposition involving a loss of oxygen. This loss of oxygen & the effect of varying conditions upon this

decomposition of manganese dioxide is now being investigated by Mr. Walker of this laboratory.

The Effect of Varying Quantities of Manganese Oxide on Potassium Permanganate.

The following experiments were made for the purpose of determining the effect of varying quantities of manganese oxide on the time required for the reduction of potassium permanganate.

A. In the presence of nitric acid.

The ratio of manganese to available oxygen in the material used for these experiments was determined and found to be

1.018 : 1.000

The experiments were conducted after the same manner as those previously described.

different portions of the manganese oxide were weighed out and heated in the flasks used in the previous experiments with the quantities of permanganate which were found by calculation to give the desired molecular ratios to the oxide. A quantity of $\frac{1}{10}$ nitric acid equivalent to the potassium of the potassium permanganate was added. The flasks were then immersed in the bath of boiling water and the time required for the disappearance of the permanganate color noted.

The ratios of the oxide to the permanganate and the times required for the reduction of the latter are embodied in the following table.

	Molecular Ratio of Oxide to $KMnO_4$	1:1	2:1	3:1	4:1	5:1	6:1	7:1
	Time of decolorization in minutes							
1	"	120	68					
2	"	110	65					
3	"	150	65					
4	"	150	80					
5	"	120	75					
6	"	125	75					
7	"	175(?)	78	53				
8	"	160	79	54				
9	"	145		41	30			
10	"	120		50	36			
11	"	?		47	32			
12	"	110			37	30		
13	"	64			(1) 20(?) 20(?)			
14	"	72			5(?)	5(?)		
15	"	85					5(?)	5(?)

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(1) Decolorized before time was taken.

The results appearing in the table on the same horizontal lines are those of experiments made simultaneously, that is the flasks in these experiments were immersed at the same time and in the same water-bath. These, that is the results appearing on the same horizontal line, and these only are comparable, since it was found that very slight differences in the temperature of the bath were of great influence on the length of time required for the reduction of the permanganate.

It is clear that the rate of the reduction of the permanganate is greatly increased by increasing the quantity of the manganese oxide.

After reduction of the permanganate the contents of the flasks were in every case filtered and the filtrate tested by

Crum's reaction for the presence of manganese. No manganese was found. The absence of manganese in the filtrate shows that the reduction of the permanganate was not due to the formation of manganese nitrate, though it will be clear from the results of subsequent experiments that the presence of nitric acid exerts no influence on the rate of the reduction.

B. In neutral solution.

The conditions were the same as under A except that the nitric acid was omitted. Three flasks containing [illegible] permanganate and one, two and seven molecular equivalents respectively of the manganese oxide were immersed in the water bath as before. No. 1 (containing one molecule of oxide and one molecule $KMnO_4$ was reduced in 57

hours

No. II {Containing two molecules of oxide and
{one molecule $KMnO_4$ was reduced in
35 hours

No. III {Containing seven molecules of oxide
{and one molecule $KMnO_4$ was reduced in
$2\frac{3}{4}$ hours

C. In alkaline solution.

The conditions were the same as under B. except that five molecules of potassium hydroxide were added for each molecule of the permanganate.

No. I {containing one molecule of oxide for
{each molecule $KMnO_4$ was reduced in
$91\frac{3}{4}$ hours.

No. II {Containing two molecules of oxide
{for each molecule $KMnO_4$ was reduced in
55(?) hours.

No. IV {Containing four molecules of oxide for each molecule $KMnO_4$ was reduced in

10 hours.

It appears that potassium permanganate is less easily reduced by manganese oxide in neutral than in acid solutions and in alkaline than in neutral solutions.

The Reduction of Neutral Potassium Permanganate by Manganese Oxide at Ordinary Temperature.

In these experiments the manganese oxide used was prepared in the same manner as that [illegible] the proportion of manganese to available oxygen was found immediately after its preparation to be

1.018 : 1.000

It was dried for several days at 65° C.,

but for almost a month after its preparation was not used. Hence what the ratio of the manganese to the oxygen was at the time when the permanganate was treated with it is quite uncertain. It however appears probable from the subsequent experiments on the solubility of manganese dioxide at 95°C. that the ratio of manganese to available oxygen must have been about 1.05 : 1.00 corresponding to a formula $MnO . 20 MnO_2$.

Two solutions of permanganate were made up, filtered through glass wool and standardized.

Solution A.

A cubic centimetre of this was found to be equivalent to 5.278 m.g. iron in the ferrous condition.

Solution B.

A cubic centimetre of this was found to be equivalent to 14.779 m.g. iron in the ferrous condition.

Three 250 c.c. portions of each of the solutions A and B were placed in clean glass stoppered bottles. These bottles were labelled a, a' and a'' b, b' and b''.

a contained 250 c.c. potassium permanganate each cubic centimetre of which was equivalent to 5.278 m.g Fe''. It was closed and put away in the dark and allowed to stand from June fourteenth until the fourteenth of the following October. Its strength was then redetermined and found to have declined 0.72 percent.

a' contained the same quantity of the same permanganate solution as a and it was closed on the same date and placed in mildly diffused light until October fourteenth. An analysis on the latter date showed that its strength had also declined 0.72 percent.

a'' contained the same quantity of the same permanganate solution as a and a' and to this was added 0.5 gram of the manganese oxide previously referred to. The bottle was then closed and placed in diffused light beside a'. An analysis October fourteenth showed that its strength had declined 34.62 percent.

b contained potassium permanganate each cubic centimetre of which was equivalent to 10.379 mg. Fe. It was closed and put away in the dark beside a. An analysis October fourteenth showed that its strength had declined 1.71 percent.

b' contained the same quantity of the same permanganate as b. It was closed and placed in mildly diffused light beside a'. An analysis October four

showed a decline in strength of [illegible] percent.

c contained the same quantity of the same permanganate as c and b'. To it was added 0.5 grams of the manganese oxide. The bottle was closed and placed in diffused light beside a' a'' and b'. The analysis [illegible] [illegible] showed a decline in strength of 78.86 percent.

The conclusions to be drawn from the foregoing results are (1) that dilute solutions of potassium permanganate are more stable both in diffused light and in darkness than the more concentrated ones, and (2) that the presence of manganese oxides hasten to an enormous degree the reduction of potassium permanganate even at summer temperatures. It will also be observed that this reducing action

of the manganese oxide is greater in the stronger than in the more dilute solutions. It should be remarked that the Summer of 1892 in which these experiments were made was one of unusual heat.

Action of Potassium Permanganate upon a Manganese Oxide derived from Manganese Dioxide by Spontaneous Decomposition.

The oxide used in these experiments was one which had been prepared in the manner heretofore described by adding manganese sulphate to an excess of potassium permanganate. Soon after its preparation the ratio of manganese to available oxygen in it was found to be

1.018 : 1.000

At the time when it was used in these experiments the ratio of manganese to available oxygen was found to be

$1.198 : 1.000$

corresponding very nearly to the ratio of manganese to available oxygen in

$MnO . 5MnO_2$.

Experiment I.

250 m.g. of the oxide was treated with the quantity of permanganate calculated to be necessary for its oxidation to manganese dioxide. The mixture was kept at a temperature of 22°c. until the color of the permanganate disappeared. This required about two hours.

An analysis of the oxide then gave a ratio of manganese to available oxygen

$1.027 : 1.000$

Experiment II

A repetition of experiment I. An analysis of the oxide after decolorization of the permanganate gave a ratio of manganese to available oxygen of

1.022 : 1.000

Experiment III

The conditions are the same as in the preceding experiments except that twice the amount of permanganate calculated for the conversion of the oxide into manganese dioxide was added.
An analysis of the residue after decolorization gave a ratio of manganese to available oxygen of

0.994 : 1.000

Experiment IV

A repetition of experiment III. An analysis of the residue gave a

ratio of manganese to available oxygen of

0.995 : 1.000

Experiment V

A repetition of experiments III and IV. The ratio of manganese to available oxygen in the residue was

0.995 : [illegible].

The foregoing results indicate (experiments III, IV, and V) that the oxygen lost spontaneously by manganese dioxide prepared in the wet way is fully recovered when the reduced oxide is treated with excess of potassium permanganate.

The ratio of the manganese to the available oxygen was determined in the following manner. The contents of the flask were filtered through asbestos and the flask and the precipitate washed with cold water. The contents of the

filter were then returned to the flask and heated with an excess of a standard solution of oxalic acid and dilute sulphuric acid. After reduction the excess of the oxalic acid was determined by a standard solution of potassium permanganate.

The solution was then filtered and washed and the manganese in the filtrate precipitated by the method of Gibbs. From the total amount of manganese found there was deducted the quantity which was introduced in determining the excess of oxalic acid by potassium permanganate.

Summary of Conclusions –

I

Potassium permanganate in weakly acid, in neutral, and in alkaline solutions, is reduced by manganese dioxide which has been prepared in the wet way with evolution of one and one half atoms of oxygen for each molecule of the permanganate. In other words, the permanganate is reduced to manganese dioxide.

II

This reduction is most rapid in acid and slowest in alkaline solutions.

III

The rate of reduction is greatly increased by increasing the proportion of manganese dioxide.

IV

In concentrated solutions of potassium permanganate the reduction by manganese dioxide is relatively more rapid than in dilute.

V

Manganese oxide prepared in the wet way i.e. by the addition of manganese sulphate to a hot solution containing excess of permanganate has the composition MnO_2 as regards the ratio of manganese to available oxygen.

VI

This oxide is unstable. It loses oxygen spontaneously even at ordinary temperatures.

VII

The oxygen which it thus lost is regained when the oxide is again heated with an excess of potassium permanganate.

VIII

It is suggested that a partial explanation of the reduction of potassium permanganate by manganese oxide may be found in the instability of the latter; in other words that the reduction may consist in alternate reduction and reoxidation processes. But when the rapidity of the reduction is taken into account it seems probable that a reaction analogous to that between permanganic acid and hydrogen peroxide must also take place.

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